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(54) Title: LIQUID COMPOSITION WITH ENHANCED LOW TEMPERATURE STABILITY

(57) Abstract

The invention relates to liquid cleansing compositions in lamellar phase. Use of minimum amounts of defined polymeric hydrophilic emulsifier in combination with a lamellar phase inducing structurant has been found to enhance both initial viscosity and free thaw (low temperature) viscosity/stability.

LIQUID COMPOSITION WITH ENHANCED LOW TEMPERATURE STABILITY

The present invention relates to liquid cleansing compositions of the type typically used in skin cleansing or shower gel compositions, which compositions are lamellar phase compositions. Such lamellar compositions are characterized by high zero shear viscosity (i.e. good for suspending) whilst simultaneously being very shear thinning, such that they readily dispense in pouring.

The rheological behavior of all surfactant solutions, including liquid cleansing solutions, is strongly dependent on the microstructure, i.e., the shape and concentration of micelles or other self-assembled structures in solution.

When there is sufficient surfactant to form micelles (i.e. the concentrations are above the critical micelle concentration or CMC), for example spherical, cylindrical (rod-like) or discoidal micelles may form. As the surfactant concentration increases, ordered liquid crystalline phases such as lamellar phase, hexagonal phase or cubic phase may form. The lamellar phase, for example, consists of alternating surfactant bilayers and water layers. These layers are not generally flat but fold to form submicron spherical onion like structures called vesicles or liposomes. The hexagonal phase, on the other hand, consists of long cylindrical micelles arranged in a hexagonal lattice. In general, the microstructure of most personal care products consist of either spherical micelles, rod micelles, or a lamellar dispersion.

As noted above, micelles may be spherical or rod-like. Formulations having spherical micelles tend to have a low

To form such lamellar compositions, however, some compromises have to be made. First, generally higher amounts of surfactant are required to form the lamellar phase. Thus, it is often needed to add auxiliary surfactants and/or salts, which are neither desirable nor needed. Secondly, only certain surfactants will form this phase and, therefore, the choice of surfactants is restricted.

In short, lamellar compositions are generally more desirable (especially for suspending emollient, and for providing consumer aesthetics), but more expensive in that they generally require more surfactant, and are more restricted in the range of surfactants that can be used.

When rod-micellar solutions are used, they also often require the use of external structurants to enhance viscosity and to suspend particles (again, because they have lower zero shear viscosity than lamellar phase solutions). For this, carbomers and clays are often used. At higher shear rates (i.e. as in product dispensing, application of the product to the body, or rubbing between the hands), since the rod-micellar solutions are less shear thinning, the viscosity of the solution stays high, and the product can be stringy and thick. Lamellar dispersion based products, having higher zero shear viscosity, can more readily suspend emollients, and are typically more creamy. Again, however, they are generally more expensive to make (e.g., they are restricted as to which surfactants can be used, and often require greater concentration of surfactants).

wishing to be bound by theory, this may be because, in cold conditions, the oil droplets become less flexible, and the spherical structure characterizing the lamellar interaction breaks into lamellar sheets instead.

Unexpectedly, the applicants have now found that certain polymeric emulsifiers, particularly hydrophilic groups modified on one or both ends, preferably both ends, by polyhydroxy fatty acid ester hydrophobic chains (e.g., dipolyhydroxystearate), can be used at small levels to enhance both initial viscosity and low temperature viscosity, thereby providing much more stable compositions.

In a first aspect, the invention comprises a liquid cleansing composition comprising:

(a) 5% to 50% by wt. of a surfactant system comprising:
   (i) at least one anionic surfactant or a mixture of anionic surfactants (e.g., 0.5 to 25% by wt.); and
   (ii) preferably an amphoteric and/or zwitterionic surfactant (e.g., betaine) or mixtures thereof (e.g., 0.1 to 25% by wt.);

(b) 0.1% to 15% by wt., preferably 1% to 10% by wt. of a lamellar phase inducing structurant selected from the group consisting of:
   (i) C_8 to C_{24} unsaturated and/or branched liquid fatty acid or ester thereof;
   (ii) C_8 to C_{24} unsaturated and/or branched liquid alcohol or ether thereof; and
   (iii) C_5 to C_9 saturated fatty acids;

Figure 1 shows effect of the polymeric hydrophilic emulsifier of invention when used in combination with lamellar phase inducing structurant. The emulsifier enhances both initial and freeze-thaw viscosity compared to use of structurant with no emulsifier.

Figure 2 shows that, for a given level of lamellar inducing structurant (e.g., isostearic acid at 5%), use of emulsifier (e.g., Arlacel P135) has no significant negative impact on lather production.

Figure 3A and 3B shows that, although it is possible to improve initial and freeze-thaw viscosity by increasing level of isostearic acid, for example, in combination with 0.5% Arlacel P135 (Figure 3A), the additional isostearic acid added to constant small level of Arlacel P135 will negatively impact on lather volume (Figure 3B). Therefore, to improve both stability without effecting lather volume, the focus should be on using emulsifier rather than increasing lamellar inducing structurant.

Figure 4 is a schematic structure of a typical polymeric emulsifier, PEG-30 dipolyhydroxystearate.

The present invention relates to liquid cleansing compositions, particularly lamellar structured liquid cleansing compositions comprising:

(a) 5% to 50% by wt. of a surfactant system comprising one or more anionic surfactants and preferably further comprising an amphoteric and/or zwitterionic surfactant or mixtures thereof;

The surfactant system of the subject invention comprises 5 to 50% by weight, preferably 10 to 40% by wt. of the composition and comprises:

(a) one or more anionic surfactants;

(b) amphoteric and/or zwitterionic surfactant; and

(c) an optional nonionic surfactant

The anionic surfactant may be, for example, an aliphatic sulfonate, such as a primary alkane (e.g., C_8-C_{22}) sulfonate, primary alkane (e.g., C_8-C_{22}) disulfonate, C_8-C_{22} alkene sulfonate, C_8-C_{22} hydroxyalkane sulfonate or alkyl glyceryl ether sulfonate (AGS); or an aromatic sulfonate such as alkyl benzene sulfonate.

The anionic may also be an alkyl sulfate (e.g., C_{12}-C_{18} alkyl sulfate) or alkyl ether sulfate (including alkyl glyceryl ether sulfates). Among the alkyl ether sulfates are those having the formula:

$$RO(CH_2CH_2O)_nSO_3M$$

wherein R is an alkyl or alkenyl having 8 to 18 carbons, preferably 12 to 18 carbons, n has an average value of greater than 1.0, preferably between 2 and 3; and M is a solubilizing cation such as sodium, potassium, ammonium or substituted ammonium. Ammonium and sodium lauryl ether sulfates are preferred.

The anionic may also be alkyl sulfosuccinates (including mono- and dialkyl, e.g., C_6-C_{22} sulfosuccinates);

wherein n = 1 to 20; and M is as defined above.

Sarcosinates are generally indicated by the formula $RCON(CH_3)CH_2CO_2M$, wherein R ranges from C_8 to C_{20} alkyl and M is a solubilizing cation.

Taurates are generally identified by formula

$$R^2CONR^3CH_2CH_2SO_3M$$

wherein R^2 ranges from C_8-C_{20} alkyl, R^3 ranges from C_1-C_4 alkyl and M is a solubilizing cation.

Another class of anionics are carboxylates such as follows:

$$R-(CH_2CH_2O)_nCO_2M$$

wherein R is C_8 to C_{20} alkyl; n is 0 to 20; and M is as defined above.

Another carboxylate which can be used is amido alkyl polypeptide carboxylates such as, for example, Monteine LCQ(R) by Seppic.

Another surfactant which may be used are the C_8-C_{18} acyl isethionates. These esters are prepared by reaction between alkali metal isethionate with mixed aliphatic fatty acids having from 6 to 18 carbon atoms and an iodine value of less than 20. At least 75% of the mixed fatty acids have from 12

sulfate, phosphate, or phosphonate. A general formula for these compounds is:

$$\begin{array}{l} \quad (R^3)_x \\ \quad\;\; | \\ R^2\text{-}Y^{(+)}\text{-}CH_2\text{-}R^4Z^{(-)} \end{array}$$

wherein R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moieties; Y is selected from nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of such surfactants include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;

5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;

3-[P,P-diethyl-P-3,6,9-trioxatetradexocylphosphonio]-2-hydroxypropane-1-phosphate;

3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;

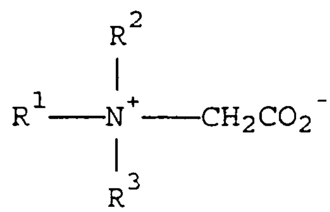
3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;

3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;

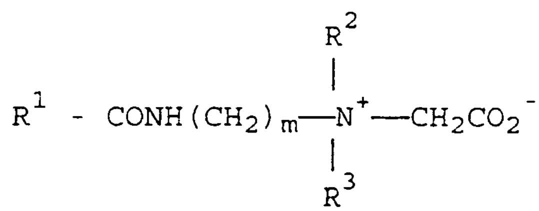
4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;

Y is $-CO_2-$ or $-SO_3-$

Suitable amphoteric detergents within the above general formula include simple betaines of formula:



and amido betaines of formula:



where m is 2 or 3.

In both formulae R^1, R^2 and R^3 are as defined previously. R^1 may in particular be a mixture of C_{12} and C_{14} alkyl groups derived from coconut so that at least half, preferably at least three quarters of the groups R^1 have 10 to 14 carbon atoms. R^2 and R^3 are preferably methyl.

A further possibility is that the amphoteric detergent is a sulphobetaine of formula:

A preferred surfactant system of the invention comprises acyl isethionate in combination with betaine (e.g., cocoamido propylbetaine).

The surfactant system may optionally comprise a nonionic surfactant.

The nonionic which may be used includes in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

The nonionic may also be a sugar amide, such as a polysaccharide amide. Specifically, the surfactant may be one of the lactobionamides described in U.S. Patent No. 5,389,279 to Au et al. which is hereby incorporated by reference or it may be one of the sugar amides described in Patent No. 5,009,814 to Kelkenberg, hereby incorporated into the subject application by reference.

Other surfactants which may be used are described in U.S. Patent No. 3,723,325 to Parran Jr. and alkyl

(e.g., emollient particles) while still maintaining good shear thinning properties. The lamellar phase also provides consumers with desired rheology ("heaping").

More particularly, where the composition is not lamellar structured and enhanced particle suspension/enhancing is desired, it is usually necessary to add external structurants such as carbomers (e.g., cross-linked polyacrylate such as Carbopol(R)) and clays. However, these external structurants have poorer shear thinning properties that significantly reduce consumer acceptability.

The structurant is generally an unsaturated and/or branched long chain (C_8-C_{24}) liquid fatty acid or ester derivative thereof; and/or unsaturated and/or branched long chain liquid alcohol or ether derivatives thereof. It may also be a short chain saturated fatty acid such as capric acid or caprylic acid. While not wishing to be bound by theory, it is believed that the unsaturated part of the fatty acid of alcohol or the branched part of the fatty acid or alcohol acts to "disorder" the surfactant hydrophobic chains and induce formation of lamellar phase.

Examples of liquid fatty acids which may be used are oleic acid, isostearic acid, linoleic acid, linolenic acid, ricinoleic acid, elaidic acid, arichidonic acid, myristoleic acid and palmitoleic acid. Ester derivatives include propylene glycol isostearate, propylene glycol oleate, glyceryl isostearate, glyceryl oleate and polyglyceryl diisostearate.

$$[CH_3(CH_2)_5\underset{\displaystyle OH}{\underset{|}{CH}}(CH_2)_{10}COOH]_i;$$

wherein i may vary from 1 to 50.

Figure 4 provides a schematic structure of a typical emulsifier which might be used having a polyalkylene glycol backbone as noted above and modified at both ends with hydrophobic groups (e.g., polyhydroxystearate) wherein number of groups at each end could vary from 1 to 50.

One example such an emulsifier which serves particularly well in the subject invention is PEG-30 dipolyhydroxystearate which is also known under the tradename Arlacel P135$^{(R)}$ ex ICI. As noted, the number of repeating alkylene groups on the chain could vary from 2 to 60 and attached hydrophobic groups may be other polyhydroxy fatty acid esters, wherein the number of groups at each end varies from 1 to 50.

A particularly good combination of the invention providing enhanced initial and freeze-thaw viscosity comprises use of isostearic acid in combination with PEG-30 dipolyhydroxystearate.

When isostearic acid alone, for example, is used as lamellar inducing structurant, the initial viscosity is about 40,000 cps, but when subjected to freeze-thaw tests when temperature is lowered (i.e., to be about -9.4°C(15F)) and raised (i.e., to room temperature), the viscosity remains the same or lower.

Other examples of oils/emollients include mineral oil, petrolatum, silicone oil such as dimethyl polysiloxane, lauryl and myristyl lactate.

It should be understood that where the emollient may also function as a structurant, it should not be doubly included such that, for example, if the structurant is 15% oleyl alcohol, no more than 5% oleyl alcohol as "emollient" would be added since the emollient (whether functioning as emollient or structurant) never comprises more than 20%, preferably no more than 15% of the composition.

The emollient/oil is generally used in an amount from about 1 to 20%, preferably 1 to 15% by wt. of the composition. Generally, it should comprise no more than 20% of the composition.

In addition, the compositions of the invention may include optional ingredients as follows:

Organic solvents, such as ethanol; auxiliary thickeners, such as carboxymethylcellulose, magnesium aluminum silicate, hydroxyethylcellulose, methylcellulose, carbopols, glucamides, or Antil$^{(R)}$ from Rhone Poulenc; perfumes; sequestering agents, such as tetrasodium ethylenediaminetetraacetate (EDTA), EHDP or mixtures in an amount of 0.01 to 1%, preferably 0.01 to 0.05%; and coloring agents, opacifiers and pearlizers such as zinc stearate, magnesium stearate, TiO_2, EGMS (ethylene glycol monostearate) or Lytron 621 (Styrene/Acrylate copolymer); all of which are useful in enhancing the appearance or cosmetic properties of the product.

Another optional ingredient which may be added are the deflocculating polymers such as are taught in U.S. Patent No. 5,147,576 to Montague, hereby incorporated by reference.

Another ingredient which may be included are exfoliants such as polyoxyethylene beads, walnut sheets and apricot seeds

The invention will now be described in greater detail by way of the following non-limiting examples. The examples are for illustrative purposes only and not intended to limit the invention in any way. All percentages in the specification and examples are intended to be by weight unless stated otherwise.

EXAMPLES

Tests relating to use of polymeric emulsifier in lamellar structured shower gel compositions where conducted in the following base compositions:

Base

Ingredient	% by Wt.
Anionic Surfactant	10 - 20%
Amphoteric Surfactant (e.g., betaine)	1 - 15%
Oil/Emollient (e.g., Sunflower Seed Oil; Silicone; Petrolatum)	0.1 - 10%
Opacifier/Colorant	0 - 2%
Perfume/Preservative	0 - 3%
Lamellar Inducing Structurant (e.g., Isostearic Acid)	1 - 8%
Hydrophilic Emulsifier (e.g., Arlacel P135)	0.5 - 5%, preferably about 1%

product in the cup should be at least 7.6cm(3 inches). The temperature of the product should be 25°C.

6. Lower the spindle into the product (~6.4mm (1/4 inches)). Set the adjustable stops of the helipath stand so that the spindle does not touch the bottom of the plastic cup or come out of the sample.

7. Start the viscometer and allow the dial to make one or two revolutions before turning on the helipath stand. Note the dial reading as the helipath stand passes the middle of its downward traverse.

8. Multiply the dial dreading by a factor of 4,000 and report the viscosity reading in cps.

EXAMPLE 1

Using the base noted above, the applicants prepared compositions comprising base, oil, Arlacel P135 and isostearic acid as noted below and obtained viscosity results at both normal (room temperature) and accelerated conditions as follows:

As can be seen from the data, when no Arlacel P135 was used (Comparatives A, B, C and D), both initial viscosity and freeze-thaw viscosity were significantly lower compared to use of small amounts of Arlacel (A versus 1 & 2; B versus 3, C versus 4, and D versus 5).

As noted, this was true no matter which oil was used.

EXAMPLE 2

Again using a composition noted above, the applicants tested for both initial and low temperature viscosity enhancement in compositions comprising varying levels of active (PEG-30 dipolyhydroxystearate) and isostearic acid. Either levels of emulsifier or lamellar inducing structurant can be varied although preferably it is level of emulsifier which is varied to ensure foam volume is maintained.

As noted in Figure 1, use of even low levels of dipolyhydroxystearate resulted in significant improvements in both initial and freeze-thaw viscosity compared to use of isostearic acid alone where viscosity remained low and certainly was not enhanced following freeze-thaw treatment.

It should be noted that 40,000 cps (seen in Figure 1 as a dotted line) is minimum target for acceptable rheology and aesthetic pleasing according to the subject invention.

EXAMPLE 3

Applicants tested effect of isostearic acid versus Arlacel P135 as shown in Figure 2.

constant small level of emulsifier, lather volume is effected (Figure 3B).

Thus, in preferred embodiments of invention, focus is on using more emulsifier rather than just increasing lamellar inducing structurant.

3. A composition according to claim 1 or 2, wherein (a)(ii) is an amphoteric surfactant which is betaine.

4. A composition according to any of claims 1 to 3, wherein the structurant is isostearic acid.

5. A composition according to any of claims 1 to 4, wherein the emulsifier is dipolyhydroxy C_{12}-C_{24} fatty acid ester.

6. A composition according to claim 5, wherein the emulsifier is dipolyhydroxystearate.

7. A composition according to any of claims 1 to 4, wherein the emulsifier is a polyalkylene glycol backbone chain of general formula:

$H(O(CH_2)_a)_nOH$

wherein a is 2 to 4 and

n is 2 to 60

having 1 to 50 C_8 to C_{24} fatty acid group or groups attached to one or both sides of the backbone.

8. A composition according to claim 7, wherein the fatty acid group or groups attached to backbone chain is hydrostearic acid.

9. A composition according to any of claims 1 to 8, wherein initial viscosity is greater than 75,000 cps.

10. A composition according to claim 9, wherein initial viscosity is 90,000 to 135,000 cps.

Fig.1.

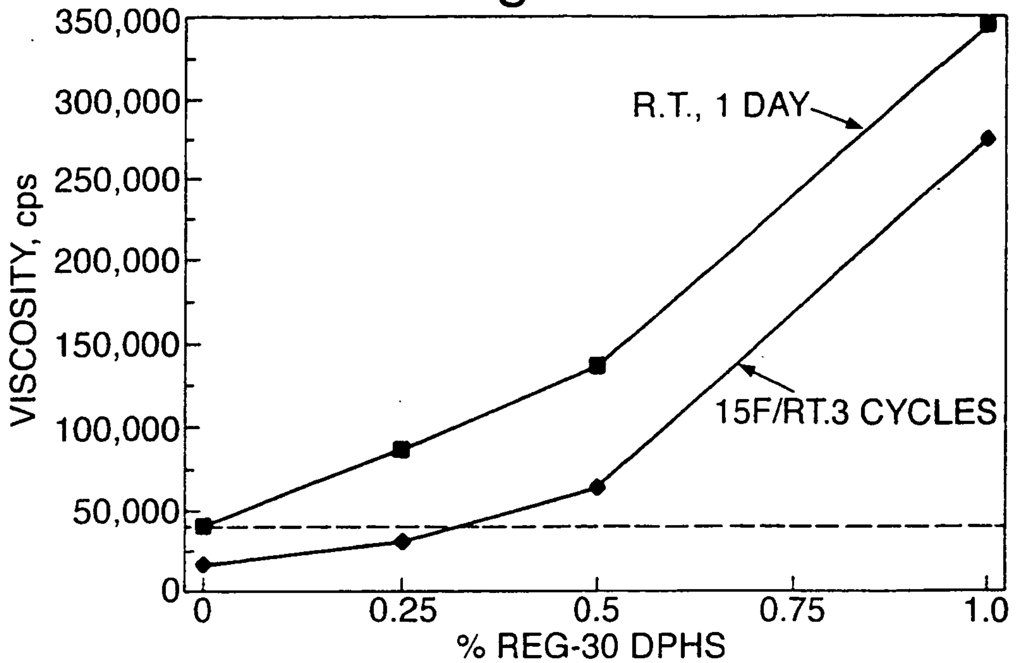
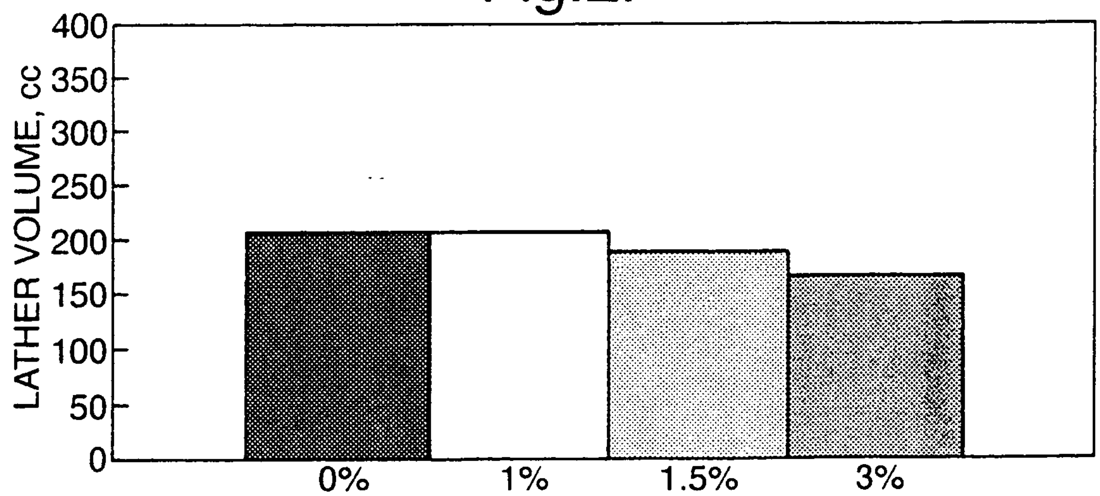


Fig.2.

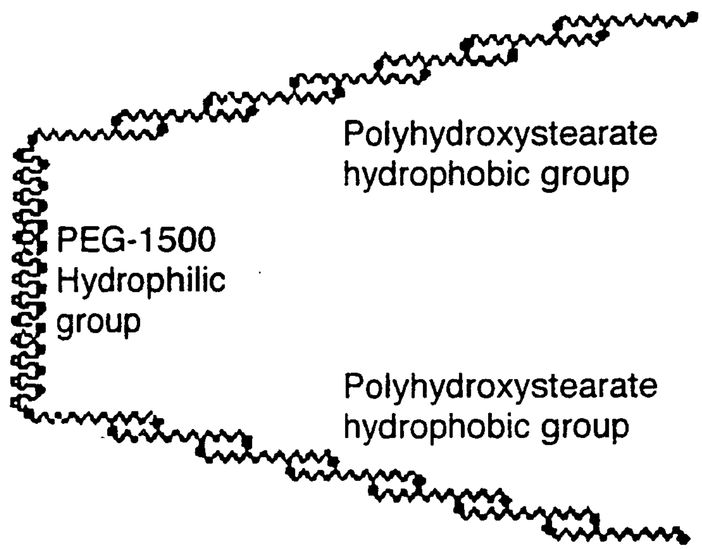


% ISOSTEARIC ACID	5.0
0% ARLACEL P135	207
1% ARLACEL P135	207
1.5% ARLACEL P135	190
3% ARLACEL P135	167

Fig.4.

INCI Name: PEG-30 Dipolyhydroxystearate
(Trade Name: Arlacel P135 ex-ICI)

SCHEMATIC STRUCTURE



Where the hydrophilic group, n, can vary from 2 to 60 and the hydrophobic group (hydroxystearate) can vary from from 1 to 50

Fig.1.

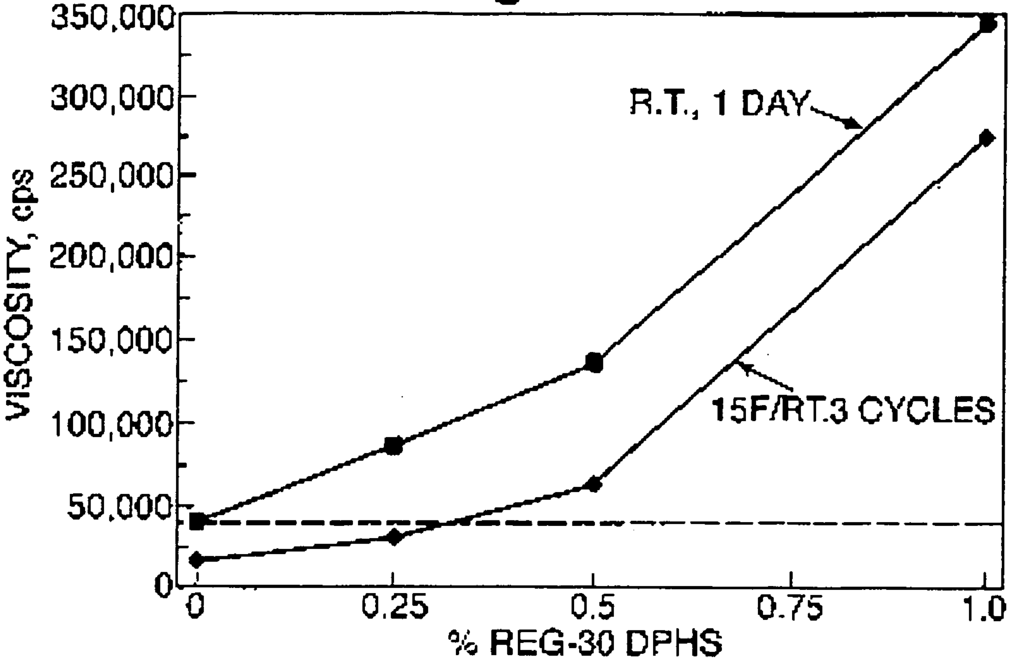
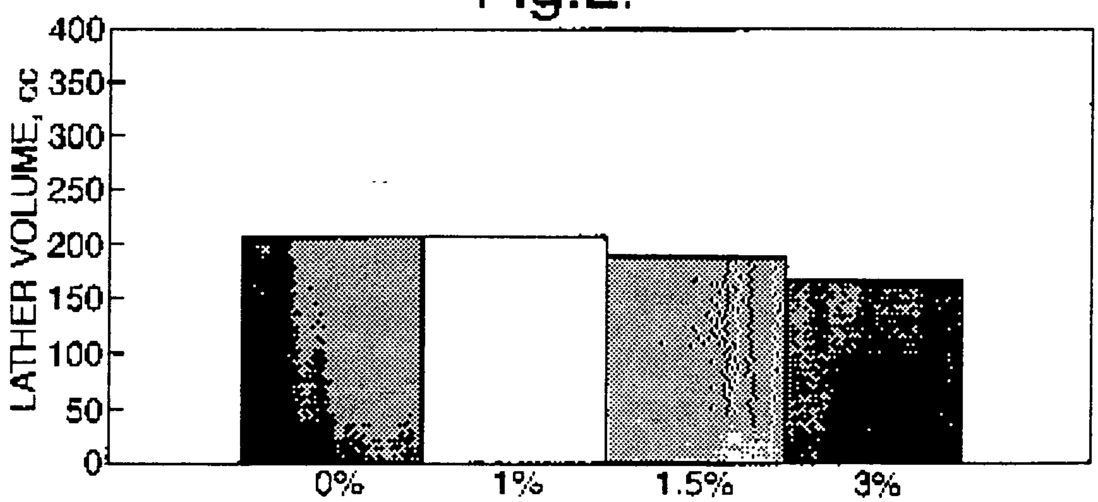


Fig.2.



% ISOSTEARIC ACID	5.0
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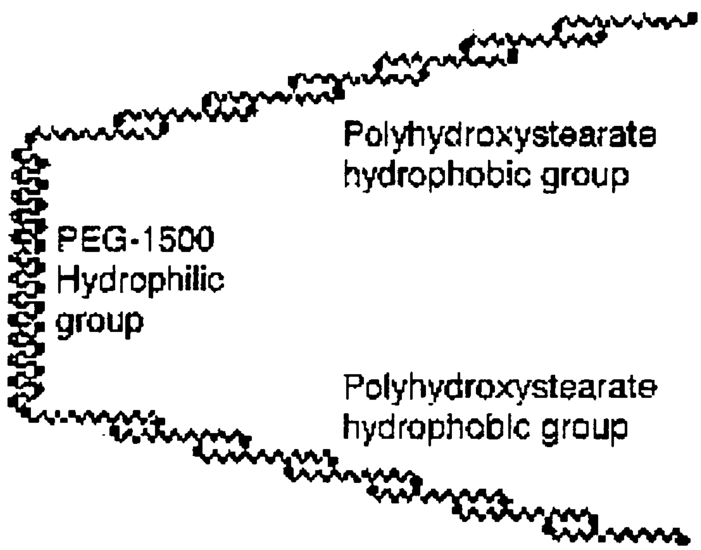
1.5% ARLACEL P135 ▒	190
3% ARLACEL P135 ▒	167

Fig.4.

INCI Name: PEG-30 Dipolyhydroxystearate
(Trade Name: Arlacel P135 ex-ICI)

SCHEMATIC STRUCTURE



Where the hydrophilic group, n, can vary from 2 to 60 and the hydrophobic group (hydroxystearate) can vary from from 1 to 50